Supporting Information for Intersystem Crossing in Diplatinum Complexes

Table S1. Fluorescence decay times and quantum yields in microcrystalline Pt(pop-BF_2) as a function of temperature. The non-radiative decay rate is completely attributed to $^1A_{2u} \rightarrow {}^3A_{2u}$ ISC ($k_{ISC} = (1 - \phi_{fl}) / \tau_{fl}$).

Temperature [K]	τ_{fl} [ns]	Φ(Fluorescence)	k_{ISC} [10^8 s^{-1}]
5	3.22	0.88	0.372
10	3.22	0.89	0.338
30	3.22	0.89	0.329
40	3.22	0.89	0.342
50	3.20	0.90	0.319
60	3.17	0.89	0.337
70	3.16	0.89	0.336
80	3.13	0.89	0.361
90	3.11	0.88	0.382
100	3.10	0.88	0.403
110	3.09	0.85	0.482
120	3.07	0.84	0.538
130	3.04	0.82	0.608
140	3.00	0.80	0.683
150	2.96	0.76	0.811
160	2.91	0.72	0.965
170	2.84	0.68	1.11
180	2.72	0.64	1.33
190	2.62	0.58	1.59
200	2.49	0.55	1.82
210	2.35	0.50	2.12
220	2.20	0.45	2.50
230	2.05	0.41	2.88
240	1.91	0.36	3.34
250	1.73	0.32	3.92
260	1.57	0.29	4.53
270	1.40	0.25	5.40
280	1.23	0.21	6.41
290	1.09	0.18	7.53
300	0.95	0.15	8.95
310	0.83	0.13	10.5

An Alternative Formalism for Multiphonon Radiationless Transitions

Treating non-radiative decay as a multiphonon transition from thermally equilibrated vibrational levels of the $^1A_{2u}$ state into densely spaced vibrational levels of a final state, Englman and Jortner derived equation (S1) as the expression for non-radiative decay rates in the strong coupling limit, where the potential energy surface of the final state is substantially displaced from that of $^1A_{2u}$.[S1] The quantitative criterion for strong coupling is $\lambda \gg \hbar\langle\omega\rangle \tanh\left(\frac{\hbar\langle\omega\rangle}{2k_BT}\right)$.

$$k_{nr} = \frac{C^2\sqrt{2\pi}}{\hbar\sqrt{\lambda k_B T^*}}\exp\left(-\frac{E_a}{k_B T^*}\right)$$
$$T^* = \frac{\hbar\langle\omega\rangle}{2k_B}\coth\left(\frac{\hbar\langle\omega\rangle}{2k_B T}\right) \qquad \text{(S1)}$$

In equation (S1), C denotes the electronic coupling term (denoted H_{AB} in the manuscript), λ the reorganization energy, and E_a the apparent activation energy. Fitting the k_{nr} data in Table S1 (Figure S1), E_a = 2024 cm^{-1}, $\hbar\langle\omega\rangle$ = 367 cm^{-1}. Since spectroscopic evidence such as vibronic progressions indicates that $^1A_{2u}$ and $^3A_{2u}$ have similar equilibrium geometries and vibrational frequencies, they are likely weakly coupled. Equation (S1), therefore, is most consistent with decay via a strongly displaced intermediate state. Unfortunately, no information about either ΔE or λ is available from equation (S1), making it impossible to determine C and the Huang-Rhys displacement parameter $S = \lambda/\hbar\langle\omega\rangle$ in this model.

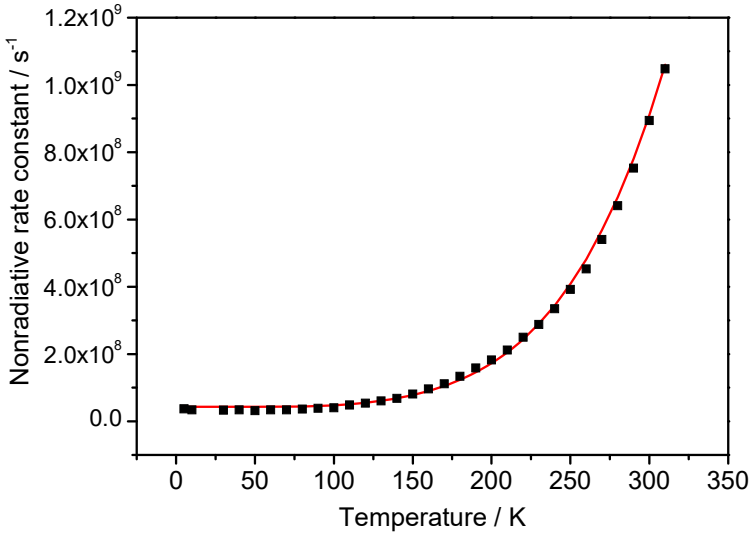

Figure S1. Temperature dependence of the nonradiative decay rate constant of the $^1A_{2u}$ excited state of Pt(pop-BF_2). Red: Fit to eq. S1: E_a = 2026 cm^{-1}; $\hbar\langle\omega\rangle$ = 367±17 cm^{-1}; $\left(C^2/\hbar\right)\left(4\pi/\lambda\hbar\langle\omega\rangle\right)^{1/2} = 2.57\times10^{12}$ s^{-1}.

Franck-Condon Analysis of Pt(pop-BF_2) Fluorescence and Minimum Linewidth Factor

Vibrational progressions in the Pt(pop-BF_2) fluorescence spectrum being associated with phonon satellites of ca. 35 cm^{-1},[S2] the reorganization energy for the lattice modes (λ) can be estimated to be 25 cm^{-1} assuming a Huang-Rhys parameter of 0.7 for the phonon modes. Since we treat lattice modes classically at all temperatures, a minimum linewidth factor (MLW) is added to the Gaussian function to avoid an infinitesimal emission linewidth at low temperature:

$$I(h\nu) = \sum_{n=0}^{\infty} \frac{S^n e^{-S}}{n!} exp\left[-\frac{(h\nu - E_{00} - n\hbar\omega)^2}{4\lambda kT + MLW}\right] \quad \text{(S1)}$$

Franck-Condon analysis of the Pt(pop-BF_2) fluorescence spectrum recorded at 10 K showed that MLW is ca. 2000 cm^{-2} (Figure S2).

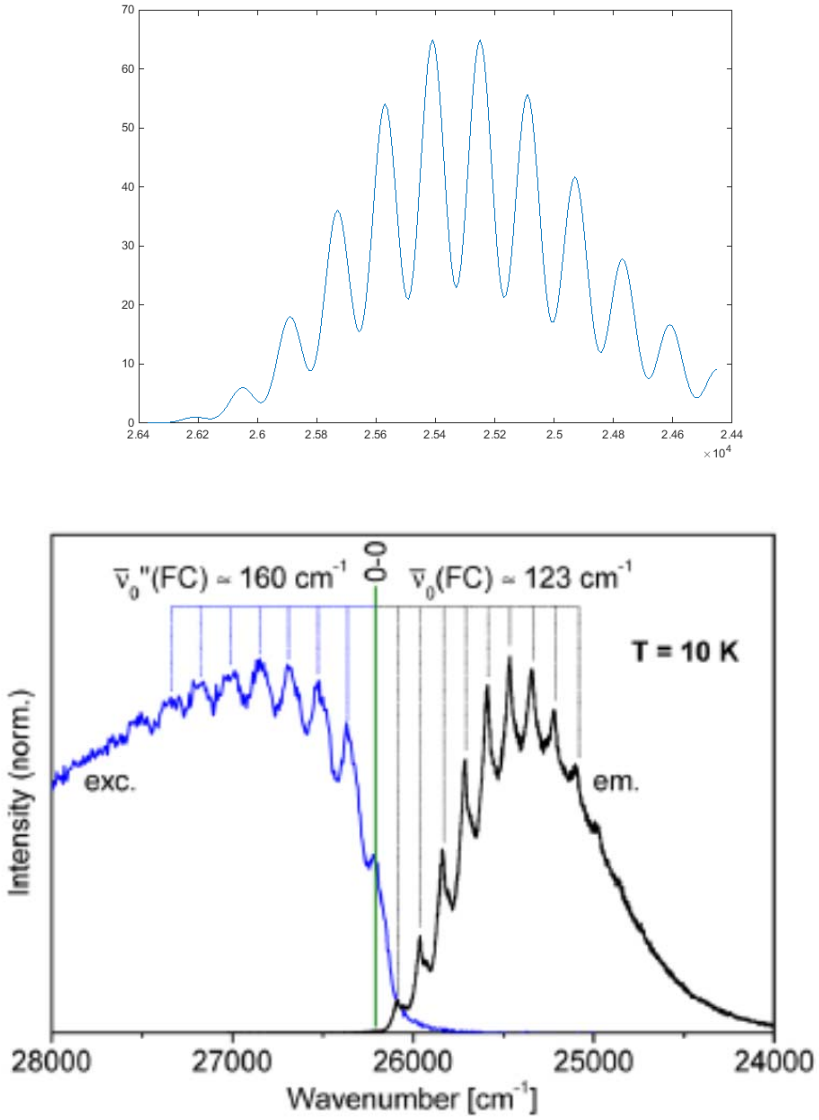

Figure S2. Top: Simulated fluorescence spectrum of Pt(pop-BF_2) at 10 K (Eq S1: S = 6, E_{00} = 26210 cm^{-1}, MLW = 2000 cm^2). Bottom: High-resolution excitation and emission spectra of Pt(pop-BF_2) at 10 K in the $^1A_{1g} \leftrightarrow {}^1A_{2u}$ energy region.[S2]

References

S1. Englman, R.; Jortner, J. *Molec. Phys.* **1970**, *18*, 145-164.
S2. Hofbeck, T.; Lam, Y. C.; Kalbac, M.; Zalis, S.; Vlcek, A.; Yersin, H., *Inorganic Chemistry* **2016**, *55*, 2441-2449.